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Synthesis, Structure, and Bonding of Stable Dialkylsilaketenimines

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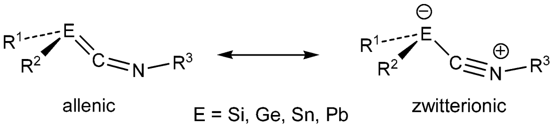
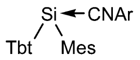
As a unique class of stable multiply bonded compounds of heavy group 14 elements, silicon, germanium, tin, and lead analogues of ketenimines have attracted much attention.[1] Their bonding characteristics are often depicted as an intermediate between two resonance structures, allenic and zwitterionic (Scheme 1) and may be significantly modified by substituents on the terminal elements.

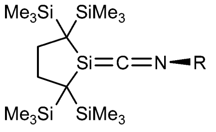
Scheme 1. Resonance Structures of R_2ECNR' Species



All known stable tin and lead analogues of ketenimines are not characterized to be allenic or zwitterionic but an isocyanide complex of the corresponding divalent species ($R_2E{\leftarrow}{:}C{=}N{-}R'$, E = Sn and Pb).[2−4] Tokitoh and co-workers were the first to synthesize silaketenimines **1a**−**1c** with bulky aryl substituents[5] and concluded that **1a**−**1c** are characterized as silylene−isocyanide complexes rather than silaketenimines on the basis of spectroscopic data, theoretical calculations, and their reactions. We wish herein to report the synthesis and X-ray structural analysis of stable dialkyl-substituted silaketenimines **2a** and **2b**, which are the first silaketenimines with strong allenic character.

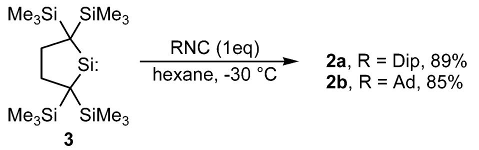


1a, Ar = Tip; **1b**, Ar = Tbt;
1c, Ar = Mes*



2a, R =Dip; **2b**, R = Ad

Silaketenimines **2a** and **2b** were synthesized by the reactions of isolable silylene **3**[6] with the corresponding isocyanides (eq 1). Typically, treatment of **3** with 1 equiv of 2,6-diisopropylphenyl isocyanide (DipNC) in hexane at −30 °C immediately gave a blue solution. Removal of the solvent in vacuo and recrystallization from hexane gave **2a** as blue crystals in 89% yield. Similarly, **2b** was obtained as red crystals in 85% yield by the reaction of **3** with 1-adamantyl isocyanide (AdNC). Both **2a** and **2b** are stable in the solid state below 0 °C but dissociate to silylene **3** and the corresponding isocyanides in solution even at low temperatures.[7,8]



3 (1)

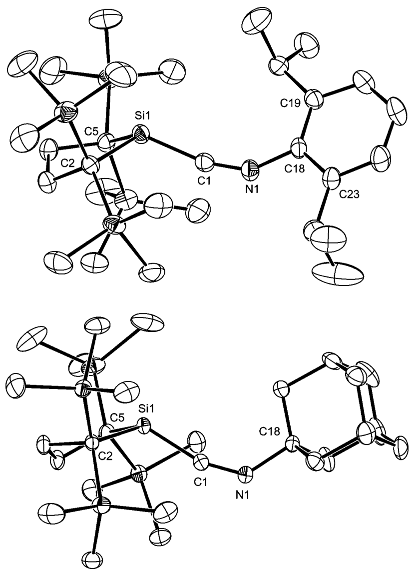


Figure 1. Molecular structures of silaketenimines **2a** (top) and **2b** (bottom). Thermal ellipsoids are shown in the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **2a**: Si1−C1 1.794(3), C1−N1 1.203(3), N1−C18 1.406(3), Si1−C1−N1 164.7(2), C1−N1−C18 146.3(3), C1−Si1−C2 113.38(12), C1−Si1−C5 116.90(13), C2−Si1−C5 100.31(12), C1−N1−C18−C19 −37.7(6), C1−N1−C18−C23 146.8(4). **2b**: Si1−C1 1.782(2), C1−N1 1.210(3), N1−C18 1.484(2), Si1−C1−N1 163.08(17), C1−N1−C18 130.69(18), C1−Si1−C2 116.49(9), C1−Si1−C5 114.37(9), C2−Si1−C5 100.73(9).

Molecular structures of **2a** and **2b** determined by X-ray analysis are shown in Figure 1.[9] The Si1−C1 bond lengths of **2a** (1.794(3) Å) and **2b** (1.782(2) Å) are remarkably shorter than a typical Si−C single bond length (1.860 Å), while being slightly longer than Si═C double bond lengths of typical silaethenes (1.693−1.764 Å).[10] The C1−N1 distances of **2a** (1.203(3) Å) and **2b** (1.210(3) Å) are much longer than the corresponding N≡C distances of aryl isocyanides (ca. 1.160 Å).[11] The C−N−C bond angles of **2a** (146.3(3)°) and **2b** (130.69(18)°) are considerably narrower than 180°, indicating that the nitrogen atom is closely sp^2-hybridized rather than sp-hybridized. All these structural parameters of **2a** and **2b** indicate that they are allenic rather than zwitterionic. Similar to that of stable trisilaallene[12] and silaallenes,[13] the Si1 atom of **2a** and **2b** is highly pyramidalized and its Si−C−N moiety adopts considerably bent geometry; the sum of the bond angles around the Si1 atom and the Si−C−N angle are 330.6(4) and 164.7(2)° and 331.6(3) and 163.08(17)° for **2a** and **2b**, respectively.

Interestingly, the bonding characteristics of **2a** and **2b** are quite different from those of silaketenimines **1a**−**1c** reported by Tokitoh et al. Whereas no X-ray analysis has been reported for **1a**−**1c**, these compounds were concluded to be silylene−isocyanide complexes rather than silaketenimines. The theoretical Si−C(≡N) distances in model aryl-substituted silaketenimines **4a** and **4b** is 1.882 and 1.867 Å at the B3LYP/6-31G(d) level,[5,14] which are much longer than those of **2a** and **2b** (Table 1). In addition, the CNC skeleton

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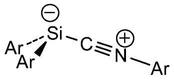
Table 1. Selected Structural Parameters of Silaketenimines

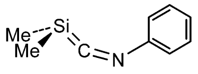
	distance/Å		angles/deg			
compd	Si–C	C–N	Si–C–N	C–N–C	δ_{Si}[a]	δ_{C}[a]
2a[b]	1.794(3)	1.203(3)	164.7(2)	146.3(3)	+15.9[c]	+214.6[c]
2b[b]	1.782(2)	1.210(3)	163.08(17)	130.69(19)	+23.9[c]	+221.3[c]
4a[d]	1.882	1.180	163.4	180.0	−	−
4b[d]	1.867	1.184	159.4	175.0	−	−
5a′[e]	1.808	1.214	164.5	135.3	+3.1	+233.6
5a″[e]	1.877	1.184	162.0	178.2	−26.8	+186.4
5b[e]	1.809	1.210	162.6	131.4	+6.4	+230.2

[a] δ_{Si} and δ_C values were calculated at the GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p) level. [b] Determined by X-ray analysis. [c] δ_{Si} and δ_C values were measured in toluene-d_8. [d] B3LYP/6-31G(d) level. See ref 5. [e] Geometry was optimized at the B3LYP/6-31+G(d,p) level.

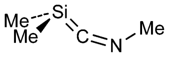
in **4a** and **4b** is almost linear with bond angles of 180.0° and 175.0°. In sharp contrast, DFT calculations for **5b** as a model for **2b** at the B3LYP/6-31+G(d,p) level reproduce the allenic character of **2b**; structural parameters for the optimized structure of **5b** are very close to those for the X-ray structure of **2b**. Interestingly, *N*-phenyl derivative **5a** shows two local minima, **5a′** and **5a″**, with different rotational conformation of the phenyl ring.[15] Compound **5a′** is only 0.7 kcal mol^{-1} more stable than **5a″** but the bonding character of **5a′** is remarkably different from that of **5a″**; **5a′** is allenic while **5a″** is zwitterionic. While the aromatic ring plane of **2a** is twisted ca. 35 ° from the Si−C−N plane, structural characteristics around the Si−C−N skeleton of **2a** are well in accord with those of **5a′**. It is concluded that bonding characteristics of silaketenimines are remarkably sensitive to the substituents. (*N*-Aryl)diarylsilaketenimines are zwitterionic but (*N*-alkyl)dialkylsilaketenimines are allenic and (*N*-aryl)dialkyl derivatives are allenic and zwitterionic depending on the rotational conformation of the *N*-aryl ring. Similar electronic substituent effects on the structure of ketenimines have been discussed by Wentrup et al.[16]



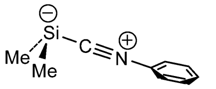
4a, Ar = Ph
4b, Ar = 2,6-dimethylphenyl



5a'



5b



5a"

The ^{29}Si and ^{13}C resonances of unsaturated silicon and carbon nuclei (δ_{Si} and δ_C) of **2a** and **2b** appear at remarkably lower fields compared to those of **1a**−**1c**; δ_{Si} values for **2a** and **2b** are +15.9 and +23.9, while δ_{Si} values for **1a**−**1c** are −48 to −58 ppm.[5] The δ_C values for **2a** and **2b** appeared at a highly deshielded region (δ_C = 214 to 221) compared with those for **1a**−**1c**. The NMR data indicate the allenic character of **2a** and **2b** in solution.[17]

Compounds **2a** and **2b** show two $\pi \rightarrow \pi^*$ absorption bands at 233 K in hexane;[8] λ_{max}/nm (ϵ): 647 (156) and 374 (6.57×10^3) for **2a** and 465 (109) and 346 (5.65×10^3) for **2b**. The longer and shorter wavelength bands are assignable to π(Si═C) → π^*(C═N) and π(Si═C) → π^*(Si═C) transitions, respectively, on the basis of TD-DFT calculations for **5a′** and **5b**.[18] Remarkable red-shift of the longer wavelength band for *N*-aryl-substituted silaketenimine **2a** would be ascribed to lowering of the π^*(C═N) orbital level due to significant π^*(C═N)−π^*(aryl) orbital interaction.[18]

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Supporting Information Available: Details for the synthesis, UV−vis spectra of**2a** and **2b**, and optimized atomic coordinates of **5a′**, **5a″**, and **5b**. X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Spectroscopic data. **2a**: blue crystals; mp < 0 °C (dec); ^1H NMR (toluene-d_8, 233 K, δ) 0.25 (s, 36H, $SiMe_3$), 1.10−1.13 (overlapping m, 14H, C*H*Me_2 and CH*Me*$_2$), 1.85 (s, 4H, CH_2), 3.65 (sept, 2 H, CH), 6.80−6.90 (m, 3H, aryl); ^{13}C NMR (toluene-d_8, 233 K, δ) 2.7, 23.9, 29.4, 34.7, 36.6, 122.6, 124.1, 130.2, 143.5, 214.6 (Si═*C*═N); ^{29}Si NMR (toluene-d_8, 233 K, δ) 3.6 ($SiMe_3$), 15.9 (*Si*═C═N, $J(^{29}Si-^{13}C)$ = 65.0 Hz); UV−vis (hexane, 233 K) λ_{max}/nm (ϵ) 647 (156), 374 (6.57×10^3), 273 (9.83×10^3). **2b**: red crystals; mp < 0 °C (dec); ^1H NMR (toluene-d_8, 233 K, δ) 0.29 (s, 36 H, $SiMe_3$), 1.50−2.10 (overlapping m, 19 H, Ad + CH_2); ^{13}C NMR (toluene-d_8, 233 K, δ) 3.1, 14.4, 23.1, 30.3, 36.5, 42.6, 221.3 (Si═*C*═N); ^{29}Si NMR (toluene-d_8, 233 K, δ) 4.5, 23.9 (*Si*═C═N); UV−vis (hexane, 233 K) λ_{max}/nm (ϵ) 465 (109), 346 (5.65×10^3).

(8) When **2a** (or **2b**) is dissolved in toluene-d_8, an equilibrated mixture of **2a** (or **2b**), silylene **3**, and the corresponding isocyanide is observed by NMR spectroscopy at temperatures higher than −30 °C. No dissociation of **2a** and **2b** is observed at −40 °C, and hence, their NMR and UV−vis data shown in ref 7 were taken at the temperature. Details of the equilibrium will be reported elsewhere.

(9) Crystal data. **2a** (−50 °C): $C_{29}H_{57}NSi_5$, FW 560.21, blue plate, monoclinic, *P*2$_1$/*n* (no. 14), a = 11.737(3) Å, b = 18.390(5) Å, c = 16.713(5) Å, β = 100.589(1)°, V = 3545.9(17) Å^3, D_{calcd} = 1.049 g/cm^3, Z = 4, $R1$ = 0.056 ($I > 2\sigma(I)$), $wR2$ = 0.139 (all data), GOF = 1.035. **2b** (−73 °C): $C_{27}H_{55}NSi_5$, FW 534.17, red prism, monoclinic, *P*2$_1$/*c* (no. 14), a = 11.2882(7) Å, b = 13.2925(7) Å, c = 22.3203(15) Å, β = 98.4590(10)°, V = 3312.7(3) Å^3, D_{calcd} = 1.071 g/cm^3, Z = 4, $R1$ = 0.057 ($I > 2\sigma(I)$), $wR2$ = 0.138 (all data), GOF = 1.31.

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(14) Whereas **4a** and **4b** were described as isocyanide complexes in ref 5, we prefer to characterize **4a** and **4b** as silaketenimines with zwitterionic character because the Si−C bond distances of **4a** and **4b** are only slightly longer than the normal Si−C single bond distance (1.86 Å).

(15) The benzene ring plane of **5a′** and **5a″** is coplanar and perpendicular to the Si−C−N plane, respectively. Compound **5a′** is characterized by the short Si−C(≡N) bond (1.808 Å), long C≡N (1.214 Å) bond, and narrow C−N−C angle (135.3 °), while **5a″** has long Si−C(≡N) bond (1.877 Å), short C−N bond (1.184 Å), and almost linear C−N−C arrangement (178.2°). See Supporting Information for details.

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(17) The $J(^{29}Si-^{13}C)$ values observed for the unsaturated Si−C bond in **2a** (65 Hz) are smaller than those for silenes (76−142 Hz)[10] but considerably larger than those of **1a**−**1c** (38.6−1.0 Hz).[5] Low-field shift of δ_{Si} and δ_C and relatively large $J(^{29}Si-^{13}C)$ indicate that **2a** and **2b** adopt allenic structure in solution.

(18) See the Supporting Information for calculation details.

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